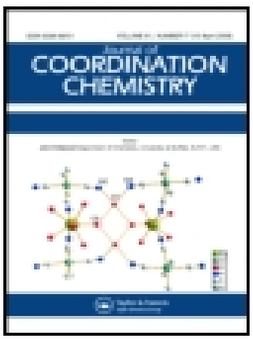

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Syntheses, characterization and catalytic activities of half-sandwich ruthenium complexes with naphthalene-based Schiff base ligands

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Four ruthenium(II) *p*-cymene complexes with naphthalene-based Schiff base ligands [Ru(*p*-cymene)LCl] (**2a**-**2d**) have been synthesized and characterized. The half-sandwich ruthenium complexes were characterized by ^{1}H and ^{13}C NMR spectra, elemental analyses and infrared spectrometry. The molecular structures of **2a**, **2b** and **2c** were confirmed by single-crystal X-ray diffraction. Furthermore, these half-sandwich ruthenium complexes are highly active catalysts for the hydrogenation of nitroarenes to anilines using $NaBH_4$ as the reducing agent in ethanol at room temperature.

Keywords: Half-sandwich; Ruthenium; Structure; Nitroarene; Reduction

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1. Introduction

Ruthenium(II)-based catalysis provides an efficient and sustainable route for organic syntheses, including transfer hydrogenation reactions of unsaturated substrates (ketone, imine and alkene) [1-4] and C-H bond activation [5, 6], which are important in synthetic organic chemistry. Many ruthenium complexes, especially half-sandwich ruthenium(II) complexes, have been widely used for these transformations [7-15]. Thus, preparation of half-sandwich ruthenium complexes and studying their catalytic properties is interesting. The half-sandwich ruthenium units with three-legged, piano-stool fragments are easy to prepare and are air-stable, where the piano-stool legs can be variably connected with N-, O-, S-, or P-donor ligands [16-25]. The majority of half-sandwich ruthenium complexes have been prepared directly *via* reaction between various organic donors and half-sandwich ruthenium dimer precursors. Schiff base compounds are important N-based ligands that are readily modifiable to allow fine tuning of steric and electronic properties of the metal center [26]. In previous studies, we have designed a series of half-sandwich ruthenium(II) complexes containing pyridyl-salicylimine; thiazol-salicylimine; benzothiazol-salicylimine and phenyl-salicylimine ligands to catalyze nitroarene reduction [27, 28]. The promising efficiency of these catalysts may be partially attributed to the strong electron-donating ability of the nitrogen and oxygen donors from Schiff base ligands.

Continuing our research in nitroarene reduction reaction catalyzed by half-sandwich ruthenium complexes, we prepare new half-sandwich ruthenium complexes with naphthalene-based Schiff base ligands and hope to exploit their chemistry in catalytic applications. In comparison with previously reported half-sandwich ruthenium systems, ruthenium catalysts containing bulky naphthalene groups may exhibit higher catalytic activity for nitroarene reduction. Preliminary results indicate that these complexes can catalyze nitroarene reduction in the presence of $NaBH_4$ in ethanol. The electronic effects on their catalytic behavior of nitroarene reduction are also discussed.

2. Experimental

2.1. *Materials and measurements*

Commercial reagents were analytical grade and used as received from Aladdin and Energy chemical. All operations were carried out under a pure nitrogen atmosphere using standard Schlenk techniques. All solvents were purified and degassed by standard procedures. The Schiff base compounds (**1a**-**1d**) and [Ru(*p*-cymene)(μ-Cl)Cl]$_2$ were synthesized according to procedures described [29-31]. ^{1}H and ^{13}C NMR spectra were recorded on a 300 MHz or 500 MHz NMR spectrometer at room temperature. Chemical shifts (δ) are given in ppm relative to internal TMS and are internally referenced to residual ^{1}H and ^{13}C solvent resonances. IR spectra were recorded on a Nicolet AVATAR-360IR spectrometer. Elemental analyses were performed on a PerkinElmer 2400 CHN analyzer.

2.2. *Synthesis*

2.2.1. Synthesis of the Schiff-bases 1a-1d

1a: 2-Hydroxy-1-naphthaldehyde (516.6 mg, 3.0 mmol) and aniline (0.273 ml, 3.0 mmol) were heated to 75 °C for 3 h in the presence of a catalytic amount of CH_3COOH (0.028 ml, 1.5 mmol) in 12 ml MeOH. The solvent was removed under reduced pressure, and the obtained solid was washed with 2 ml EtOH three times. Yellow solid; yield: (555.8 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.50 (s, 1H, O*H*), 9.30 (s, 1H, C*H*N), 8.08 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.79 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.70 (d, J = 6.0 Hz, 1H, Ar-*H*), 7.64-7.22 (m, 7H, Ar-*H*), 7.08 (d, J = 9.0 Hz, 1H, Ar-*H*); IR (KBr, cm^{-1}): 3432 (m), 2368 (m), 1622 (vs), 1594 (s), 1543 (s), 1520 (s), 1491 (s), 1346 (s), 1318 (s), 1142 (m), 838 (s), 759 (vs), 687 (s).

1b: 2-Hydroxy-1-naphthaldehyde (516.6 mg, 3.0 mmol) and p-toluidine (0.330 ml, 3.0 mmol) were heated to 75 °C for 3 h in the presence of a catalytic amount of CH_3COOH (0.028 ml, 1.5 mmol) in 12 ml MeOH. The solvent was removed under reduced pressure, and the obtained solid was washed with 2 ml EtOH three times. Yellow solid; yield: (736.0 mg, 94%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 15.62 (s, 1H, O*H*), 9.29 (s, 1H, C*H*N), 8.07 (d, J = 6.0 Hz, 1H, Ar-*H*), 7.78

(d, J = 9.0 Hz, 1H, Ar-*H*), 7.70 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.40-7.18 (m, 5H, Ar-*H*), 7.07 (d, J = 9.0 Hz, 1H, Ar-*H*), 2.39 (s, 3H, *p-Me*); IR (KBr, cm^{-1}): 3447 (m), 3023 (w), 2915 (w), 2854 (w), 1617 (vs), 1581 (s), 1540 (m), 1512 (s), 1326 (s), 968 (m), 853 (m), 815 (s), 738 (s).

1c: 2-Hydroxy-1-naphthaldehyde (516.6 mg, 3.0 mmol) and 4-chloroaniline (382.7 mg, 3.0 mmol) were heated to 75 °C for 3 h in the presence of a catalytic amount of CH_3COOH (0.028 ml, 1.5 mmol) in 12 ml MeOH. The solvent was removed under reduced pressure, and the obtained solid was washed with 2 ml EtOH three times. Yellow solid; yield: (792.4 mg, 94%). ^1H NMR (300 MHz, $CDCl_3$): δ 15.29 (s, 1H, O*H*), 9.33 (s, 1H,C*H*N), 8.10 (d, J = 6.0 Hz, 1H, Ar-*H*), 7.82 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.73 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.53 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.43-7.27 (m, 5H, Ar-*H*), 7.11 (d, J = 9.0 Hz, 1H, Ar-*H*); IR (KBr, cm^{-1}): 3447 (m), 3064 (w), 3033 (w), 1617 (vs), 1578 (m), 1563 (s), 1540 (m), 1486 (s), 1326 (s), 1165 (m), 858 (w), 820 (s), 746 (s), 723 (w).

1d: 2-Hydroxy-1-naphthaldehyde (516.6 mg, 3.0 mmol) and 4-nitroanline (414.4 mg, 3.0 mmol) were heated to 75 °C for 3 h in the presence of a catalytic amount of CH_3COOH (0.028 ml, 1.5 mmol) in 12 ml MeOH. The solvent was removed under reduced pressure, and the obtained solid was washed with 2 ml EtOH three times. Red solid; yield: (727.1 mg, 83%). ^1H NMR (300 MHz, $CDCl_3$): δ 14.87 (s, 1H, O*H*), 9.38 (s, 1H, C*H*N), 8.34 (d, J = 9.0 Hz, 1H, Ar-*H*), 8.12 (d, J = 6.0 Hz, 1H, Ar-*H*), 7.87 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.75 (d, J = 9.0 Hz, 1H, Ar-*H*), 7.56 (t, J = 9.0 Hz, 1H, Ar-*H*), 7.46-7.37 (m, 3H, Ar-*H*), 7.12 (d, J = 9.0 Hz, 1H, Ar-*H*); IR (KBr, cm^{-1}): 3444 (m), 3070 (w), 1621 (s), 1581 (s), 1547 (s), 1504 (s), 1336 (vs), 1287 (s), 1107 (s), 860 (s), 828 (s), 760 (s).

2.2.2. Synthesis of half-sandwich ruthenium complexes with naphthalene-based Schiff base ligands 2a-2d

A solution of $[Ru(p\text{-cymene})(\mu\text{-Cl})Cl]_2$ (122.4 mg, 0.20 mmol), the Schiff base (0.50 mmol, **1a** (123.5 mg), **1b** (130.6 mg), **1c** (140.5 mg), **1d** (146.0 mg)) and K_2CO_3 (69.0 mg, 0.50 mmol) in MeOH (15 mL) was purged with N_2 and then stirred for 4 h at room temperature. The reaction

mixture was separated from insoluble salts by filtration and dried *in vacuo*. The crude material was subjected to silica gel chromatography with ethyl acetate and petroleum ether (1:1) to give the dark red half-sandwich ruthenium complexes.

Chloro(*p*-cymene)(1-((phenylimino)methyl)naphthalen-2-ol-κ-O,N)ruthenium(II) **2a**: Yield: (140.6 mg, 68%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.58 (s, 1H, C*H*N), 7.69-7.56 (m, 5H, Ar-*H*), 7.53-7.44 (m, 2H, Ar-*H*), 7.36-7.25 (m, 2H, Ar-*H*), 7.19-7.10 (m, 2H, Ar-*H*), 5.37 (d, J = 6.0 Hz, 1H, *p*-Cy), 5.30 (d, J = 6.0 Hz, 1H, *p*-Cy), 4.97 (d, J = 6.0 Hz, 1H, *p*-Cy), 4.19 (d, J = 6.0 Hz, 1H, *p*-Cy), 2.62 (m, 1H, C*H*Me_2), 2.13 (s, 3H, Ar*Me*), 1.16 (d, J = 6.0 Hz, 3H, CH*Me*$_2$), 1.09 (d, J = 6.0 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 165.99, 159.62, 157.74, 135.83, 134.85, 128.86, 127.29, 126.70, 126.61, 125.40, 124.21, 121.88, 118.65, 108.16, 101.27, 97.88, 86.62, 84.35, 83.78, 80.43, 30.40, 22.82, 21.56, 18.57. Anal. Calcd. for $C_{27}H_{26}NORuCl$: C, 62.72; H, 5.07; N, 2.71. Found: C, 62.75; H, 5.10; N, 2.78. IR (KBr, cm^{-1}): 3032 (w), 2968 (w), 2870 (w), 1617 (vs), 1604 (vs), 1576 (s), 1536 (vs), 1453 (m), 1364 (s), 1179 (s), 1160 (m), 1081 (m), 835 (m), 820 (s), 745 (s), 590 (s).

Chloro(*p*-cymene)(1-((p-tolylimino)methyl)naphthalen-2-ol-κ-O,N)ruthenium(II) **2b**: Yield: (137.8 mg, 65%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.57 (s, 1H, C*H*N), 7.67 (d, J = 10.0 Hz, 1H, Ar-*H*), 7.59 (d, J = 10.0 Hz, 1H, Ar-*H*), 7.55 (d, J = 5.0 Hz, 2H, Ar-*H*), 7.31-7.24 (m, 4H, Ar-*H*), 7.16 (d, J = 10.0 Hz, 1H, Ar-*H*), 7.12 (d, J = 10.0 Hz, 1H, Ar-*H*), 5.38 (d, J = 5.0 Hz, 1H, *p*-Cy), 5.30 (d, J = 5.0 Hz, 1H, *p*-Cy), 4.97 (d, J = 5.0 Hz, 1H, *p*-Cy), 4.22 (d, J = 5.0 Hz, 1H, *p*-Cy), 2.64 (m, 1H, C*H*Me_2), 2.45 (s, 3H, Ar*Me)*, 2.16 (s, 3H, Ar*Me*), 1.18 (d, J = 5.0 Hz, 3H, CH*Me*$_2$), 1.19 (d, J = 10.0 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.29, 158.04, 157.86, 136.77, 136.07, 135.26, 129.70, 129.20, 127.61, 127.00, 125.78, 124.36, 122.19, 119.04, 108.57, 101.53, 101.49, 98.36, 87.12, 87.08, 84.74, 84.12, 80.99, 30.82, 23.21, 22.01, 21.47, 19.02. Anal. Calcd. for $C_{28}H_{28}NORuCl$: C, 63.33; H, 5.31; N, 2.64. Found: C, 63.39; H, 5.27; N, 2.70. IR (KBr, cm^{-1}): 3040 (w), 2964 (w), 2921 (w), 2870 (w), 1617 (vs), 1602 (vs), 1574 (s), 1506 (w), 1451 (m), 1362 (s), 1179 (s), 1160 (m), 1088 (m), 832 (m), 820 (m), 743 (m), 588 (m).

Chloro(*p*-cymene)(1-((4-chlorophenylimino)methyl)naphthalen-2-ol-κ-O,N)ruthenium(II) **2c**: Yield: (158.7 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.53 (s, 1H, C*H*N), 7.68-7.54 (m, 4H, Ar-*H*), 7.44 (t, J = 9.0 Hz, 2H, Ar-*H*), 7.32 (t, J = 6.0 Hz, 1H, Ar-*H*), 7.14 (t, J = 6.0 Hz, 2H, Ar-*H*), 5.39 (d, J = 6.0 Hz, 1H, *p*-Cy), 5.32 (d, J = 6.0 Hz, 1H, *p*-Cy), 4.98(d, J = 6.0 Hz, 1H, *p*-Cy), 4.26 (d, J = 6.0 Hz, 1H, *p*-Cy), 2.63 (m, 1H, C*H*Me_2), 2.15 (s, 3H, Ar*Me*), 1.18 (d, J = 6.0 Hz, 3H, CH*Me*$_2$), 1.10 (d, J = 6.0 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 166.72, 158.43, 158.30, 136.57, 135.14, 132.66, 129.34, 129.30, 127.83, 127.03, 126.05, 125.75, 122.45, 118.91, 108.54, 101.77, 98.64, 87.10, 84.57, 83.75, 80.93, 30.87, 23.16, 22.04, 19.03. Anal. Calcd. for $C_{27}H_{25}NORuCl_2$: C, 58.81; H, 4.57; N, 2.54. Found: C, 58.85; H, 4.60; N, 2.52. IR (KBr, cm^{-1}): 3036 (w), 2964 (w), 2925 (w), 2870 (w), 1615 (vs), 1602 (vs), 1581 (vs), 1504 (w), 1451 (s), 1362 (vs), 1181 (s), 1139 (m), 822 (s), 745 (s), 652 (w).

Chloro(*p*-cymene)(1-((4-nitrophenylimino)methyl)naphthalen-2-ol-κ-O,N)ruthenium(II) **2d**: Yield: (157.4 mg, 70%). ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.53 (s, 1H, C*H*N), 8.34 (d, J = 10.0 Hz, 2H, Ar-*H*), 7.87 (d, J = 10.0 Hz, 2H, Ar-*H*), 7.64 (t, J = 10.0 Hz, 2H, Ar-*H*), 7.56 (d, J = 5.0 Hz, 1H, Ar-*H*), 7.34 (t, J = 10.0 Hz, 1H, Ar-*H*), 7.17-7.14 (m, 2H, Ar-*H*), 5.40 (d, J = 5.0 Hz, 1H, *p*-Cy), 5.34 (d, J = 5.0 Hz, 1H, *p*-Cy), 4.98 (d, J = 5.0 Hz, 1H, *p*-Cy), 4.28 (d, J = 5.0 Hz, 1H, *p*-Cy), 2.62 (m, 1H, C*H*Me_2), 2.16 (s, 3H, Ar*Me*), 1.18 (d, J = 10.0 Hz, 3H, CH*Me*$_2$), 1.11 (d, J = 5.0 Hz, 3H, CH*Me*$_2$). ^{13}C NMR (125 MHz, $CDCl_3$): δ 167.59, 164.42, 158.26, 146.33, 137.38, 135.01, 129.46, 128.13, 127.12, 128.87, 125.75, 125.08, 122.85, 118.81, 108.76, 102.15, 99.10, 87.11, 84.35, 83.39, 80.91, 30.95, 23.10, 22.11, 19.05. Anal. Calcd. for $C_{27}H_{25}N_2O_3RuCl$: C, 57.70; H, 4.48; N, 4.98. Found: C, 57.68; H, 4.47; N, 5.03. IR (KBr, cm^{-1}): 3044 (w), 2972 (w), 2934 (w), 2874 (w), 1617 (s), 1602 (s), 1574 (s), 1530 (s), 1515 (s), 1455 (w), 1336 (vs), 1181 (s), 1111 (m), 820 (m), 743 (m), 588 (w).

2.2.3. General procedure for the reduction of nitroarenes to anilines with half-sandwich ruthenium catalysts

The half-sandwich ruthenium complex (0.003 mmol, 0.01 equiv) was dissolved in solvent (2.0 mL), and then the appropriate nitroarene (0.3 mmol, 1.0 equiv) and $NaBH_4$ (45.4 mg, 1.2 mmol, 4.0 equiv) were added. The resulting mixture was stirred at room temperature in a closed vessel. After completion of the reation (monitored by TLC), the crude reaction mixture was extracted with ether (3×2 mL). After the solvents were removed *in vacuo* from the combined organic extracts, the crude products were loaded directly onto a column of silica gel and purified by column chromatography using petroleum ether and ethyl acetate (1:3) to get the corresponding products [27].

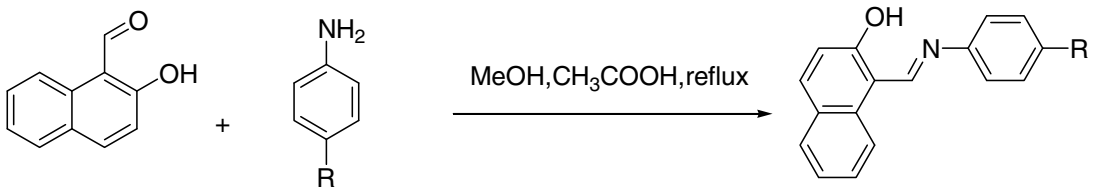
2.3. *X-ray structure determination*

Diffraction data of **2a**, **2b** and **2c** were collected on a Bruker AXS SMART APEX diffractometer equipped with a CCD area detector using Mo Kα radiation (λ = 0.71073 Å). All the data were collected at 298 K and the structures were solved by direct methods and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [32]. SADABS absorption corrections were applied to the data [33]. All non-hydrogen atoms were refined anisotropically, and hydrogens were located at calculated positions. All calculations were performed using the Bruker Smart program. A summary of the crystallographic data and selected experimental information are given in table 1. Selected bond angles and distances are given in table 2.

3. Results and discussion

3.1. *Synthesis of Schiff base compounds and half-sandwich ruthenium complexes*

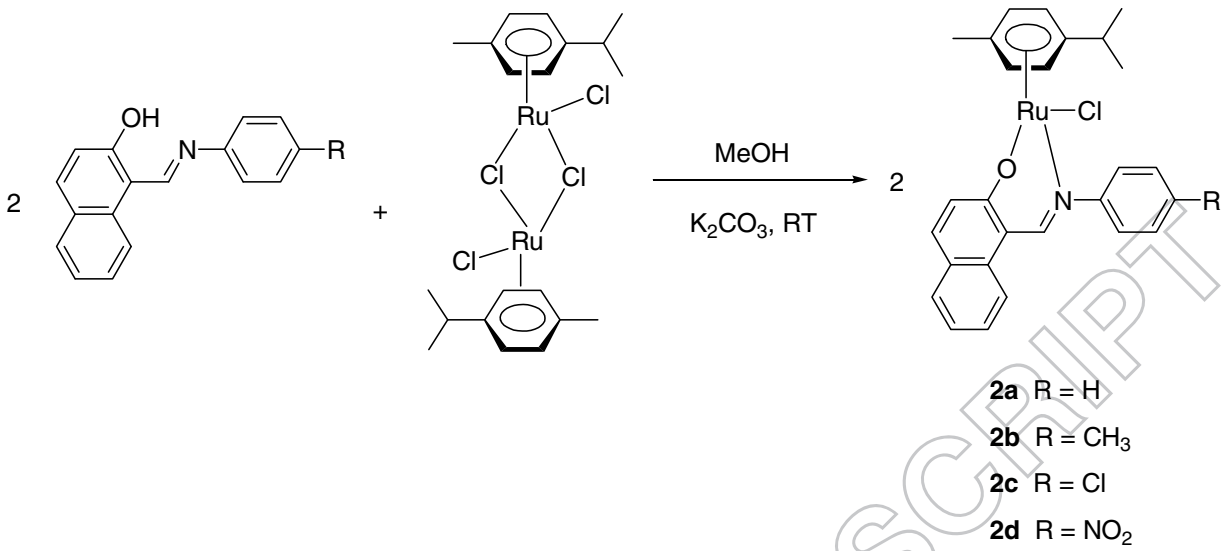
According to literature methods, the naphthalene-based Schiff base derivatives **1a**-**1d** were prepared by condensation of 2-hydroxy-1-naphthaldehyde with different p-substituted aryl amines in a 1:1 mole ratio in methanol in the presence of a catalytic amount of CH_3COOH (scheme 1) [30, 31].



1a R = H
1b R = CH_3
1c R = Cl
1d R = NO_2

Scheme 1. Synthesis of Schiff base compounds (**1a**-**1d**).

The dark red half-sandwich complexes [(*p*-cymene)LRuCl] (**2a**-**2d**) were obtained by treatment of 2 equivalents of the Schiff base (**1a**-**1d**) with [(*p*-cymene)Ru(μ-Cl)Cl]$_2$ in the presence of K_2CO_3 in MeOH at room temperature (scheme 2). The half-sandwich ruthenium complexes (**2a**-**2d**) were isolated as pure complexes by chromatography on silica gel using ethyl acetate and petroleum ether (1:1) as eluent in yields of 65-72%. All complexes have been characterized by IR and NMR spectroscopy as well as elemental analysis. The half-sandwich ruthenium complexes are air and moisture stable, soluble in chlorohydrocarbons, alcohol, and acetonitrile but insoluble in water.



Scheme 2. Synthesis of half-sandwich ruthenium complexes (**2a**-**2d**).

The ^{1}H NMR spectrum of **2d** displays a distinct resonance shift of the Schiff base ligand's protons in comparison with the equivalent protons in the free compound. The proton signals at 8.53, 8.34, 7.87, 7.64, 7.56, 7.34, 7.17, 5.40, 5.34, 4.98, 4.28, 2.62, 2.16, 1.18 and 1.11 ppm in the ^{1}H NMR spectrum can be easily assigned to each of the corresponding hydrogen atoms of **2d**. The proton signal at 14.87 ppm corresponds to the OH group of the free ligand which disappears in **2d** due to coordination. Four doublets appear at δ = 5.40, 5.34, 4.98 and 4.28 ppm with a coupling constant of J = 5.0 Hz, respectively, which indicates the presence of the cymene ring [34, 35].

X-ray diffraction of single crystals for **2a**, **2b** and **2c** were obtained. The crystals were grown by slow diffusion of diethyl ether into a concentrated solution of the complexes in methanol. The crystallographic data for **2a**, **2b** and **2c** are summarized in table 1. The molecular structures of **2a**, **2b** and **2c** are shown in figure 1. All structures were solved with monoclinic $P2_1/n$ space groups. As shown in figure 1, each ruthenium is coordinated by *p*-cymene, one nitrogen and one oxygen of the Schiff base ligand, and one chloride adopting a typical distorted piano-stool geometry. The Ru-O distances (2.0576(13) (**2a**), 2.0486(14) (**2b**) and 2.044(3) (**2c**)) and Ru-N distances (2.0857(15) (**2a**), 2.0772(16) (**2b**) and 2.078(3) (**2c**)) are consistent with

Ru-N/Ru-O bond length values reported for half-sandwich ruthenium complexes with [N,O] anionic ligands [36-39], while the Ru-N bond lengths are shorter than those of half-sandwich ruthenium complexes with diphenyl(2-pyridyl)phosphine ligands, [(*p*-cymene)Ru(S=PPh2Py)Cl]PF6 (2.123(3)) and [(benzene)Ru(PPh2Py)Cl]PF6 (2.118(4)) [40]. The flexible dihedral angles (58.53° (**2a**), 65.95° (**2b**) and 65.71° (**2c**)) between the naphthalene group and phenyl moiety of the Schiff base indicate the different special effects of different substituent groups on the phenyl ring. Significant hydrogen bonding occurs in the crystal structures of **2a**-**2c**. Their chlorides are involved in intermolecular hydrogen bonds ((Cl and H of cymene) (C(23)-C1(1) = 3.693(2) Å, C(23)-H(23)···C1(1) = 158° (**2a**); (C(24)-C1(1) = 3.587(2) Å, C(24)-H(24)···C1(1) = 145° (**2b**) and (C(21)-C1(1) = 3.579(5) Å, C(21)-H(21)···C1(1) = 145° (**2c**)). For **2a**, adjacent units are connected to form a dimer through intermolecular hydrogen bonds (figure 1(2)).

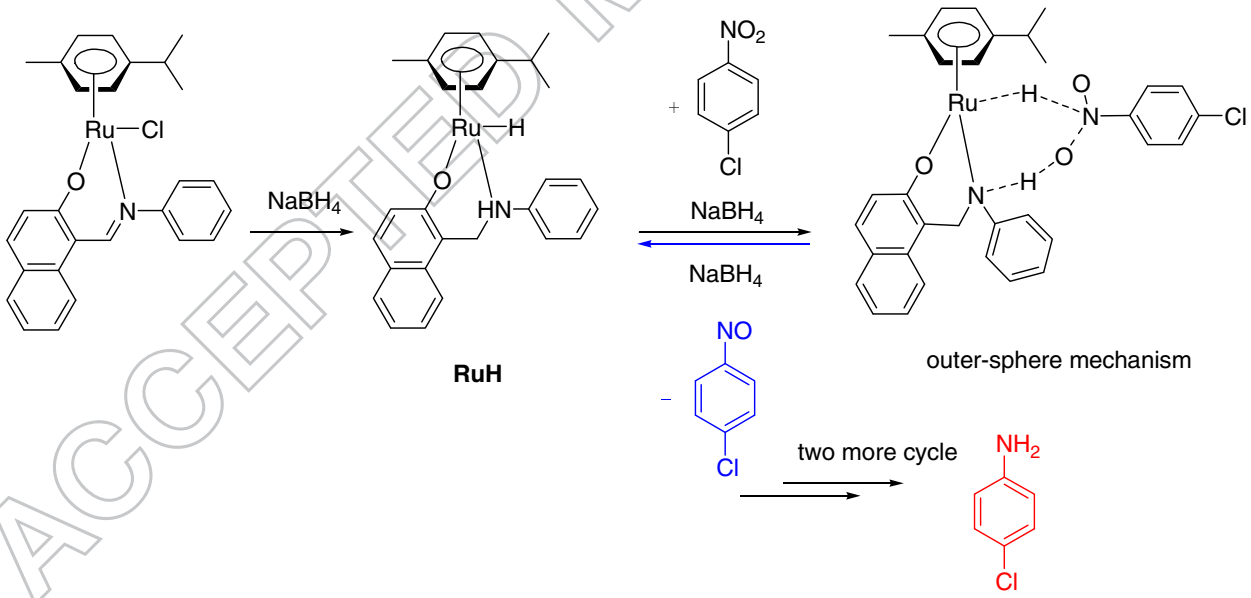
3.2. *The nitroarene reduction catalyzed by half-sandwich ruthenium complexes*

The catalytic performance of half-sandwich ruthenium complexes **2a**-**2d** has been evaluated for reduction of nitroarenes using 1-chloro-4-nitrobenzene in the presence of $NaBH_4$ (table 3). As shown in table 3, **2d** was very active towards reduction of nitroarenes. However, different activities exhibited by **2a**-**2d** suggest that electronic effects of the substituted groups influence catalyst performance. For example, **2d** with a -NO_2 exhibited higher catalytic activity than the other complexes (table 3, entries 1-4) because the electron-deficient metal center facilitated formation of the hydride intermediate. Thus **2d** was chosen as the optimal catalyst to screen various solvents (table 3, entries 5-7). No desired products were detected in water due to the poor solubility of the catalyst (table 3, entry 10). When the catalyst amount was decreased, the conversion also decreased even with a longer reaction time (table 3, entry 11). No catalytic activity was observed for nitroarene reduction without addition of a ruthenium complex (table 3, entries 8 and 9). From these studies, the optimal conditions for the reduction of nitroarenes were

using **2d** as catalyst (1 mol %) in the presence of four equivalents of $NaBH_4$ at room temperature.

With the optimal reaction condition in hand, we started to expand the scope and efficiency of this methodology. Many functionalized anilines were obtained in excellent yields (table 4). As shown in table 4, electron-withdrawing and electron-donating substituents on the aromatic ring were converted to the desired products in excellent yields. In the case of 4-nitrobenzaldehyde, the -CHO group was reduced together with the $-NO_2$ group. Under the same reaction conditions, -NHCOMe was unchanged (table 4, entries 11 and 12).

The half-sandwich ruthenium hydride active species can be confirmed through *in situ* NMR studies (δ -10.18 ppm, Supporting Information). The proton signal at -10.18 ppm corresponds to a hydride, which indicates the presence of a Ru-H intermediate [41, 42]. A possible mechanism of nitroarene reduction is an outer-sphere mechanism through a half-sandwich ruthenium hydride intermediate as previously reported (scheme 3) [28].



Scheme 3. Probable mechanism for the reduction of nitroarenes catalyzed by ruthenium complexes.

4. Conclusion

We have synthesized and characterized four half-sandwich ruthenium complexes with naphthalene-based Schiff base ligands and evaluated their ability as catalysts for nitroarene reduction in the presence of $NaBH_4$ in ethanol at room temperature. The hydrogenation of nitroarenes exhibits varied functional group compatibility and provides anilines in excellent yields. Moreover, a combination of spectroscopic studies and X-ray crystallographic studies also confirmed the molecular structure of the half-sandwich ruthenium complexes.

Appendix. Supplementary material

The crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1496634 (**2a**), CCDC-1496633 (**2b**) and CCDC-1496635 (**2c**) (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk, http://www.ccdc.cam.ac.uk).

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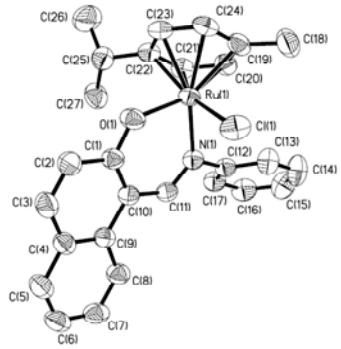
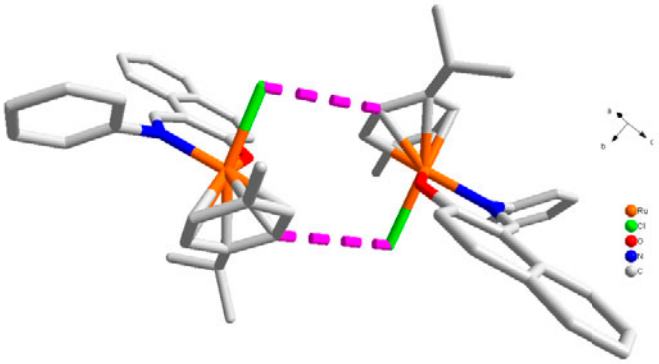


(**1**)



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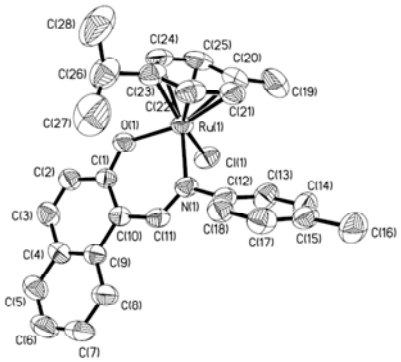

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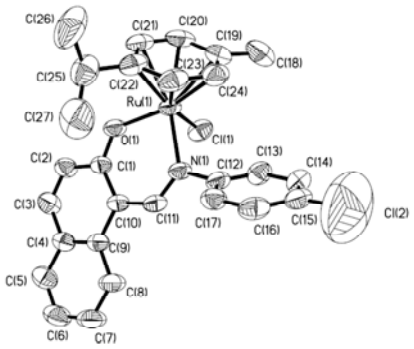


(**4**)

Figure 1. (1) Molecular structure of **2a** with thermal ellipsoids drawn at the 50% level. (2) The dimer structure connected by intermolecular hydrogen bonds in **2a**. (3) Molecular structure of **2b** with thermal ellipsoids drawn at the 50% level. (4) Molecular structure of **2c** with thermal ellipsoids drawn at the 50% level; all hydrogens are omitted for clarity.

Table 1. Crystallographic data and structure refinement parameters for ruthenium complexes.

	2a	**2b**	**2c**
Empirical formula	$C_{27}H_{26}ClNORu$	$C_{28}H_{28}ClNORu$	$C_{27}H_{25}Cl_2NORu$
Formula weight	517.01	531.03	551.45
Crystal system, Space group	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$	Monoclinic, $P2_1/n$
a (Å)	10.5933(7)	12.7524(7)	12.724(7)
b (Å)	16.1394(11)	14.8292(8)	14.803(8)
c (Å)	14.3720(10)	12.9306(7)	12.935(7)
β (°)	108.4530(10)	94.1600(10)	94.074(6)
Volume ($Å^3$), Z	2330.8(3), 8	2438.8(2), 4	2430(2), 4
D_c (mg / m^3)	1.473	1.446	1.507
μ (Mo-Kα) (mm^{-1})	0.806	0.772	0.885
F(000)	1056	1088	1120
θ range (°)	1.955 ~ 27.573	2.329 ~ 27.453	2.094 ~ 27.682
Limiting indices	-13, 13; -21, 20; -18, 18	-16, 16; -16, 18; -16, 16	-16, 16; -19, 19; -16, 16
Reflections / unique [R(int)]	5319 / 4902 [0.0507]	5454/4439 [0.0246]	5590/4861 [0.1056]
Completeness to θ (°)	27.573 (98.8 %)	27.453 (97.4%)	27.682 (98.3 %)
Data / restraints / parameters	5319 / 0 / 283	5454 / 0 / 293	5590 / 0 / 286
Goodness-of-fit on F^2	1.062	1.028	1.088
R_1, wR_2 $[I > 2\sigma(I)]$[a]	R_1= 0.0253, wR_2= 0.0644	R_1= 0.0278, wR_2= 0.0665	R_1= 0.0751, wR_2= 0.2340
R_1, wR_2 (all data)	R_1= 0.0282, wR_2= 0.0672	R_1= 0.0389, wR_2= 0.0719	R_1= 0.0834, wR_2= 0.2442

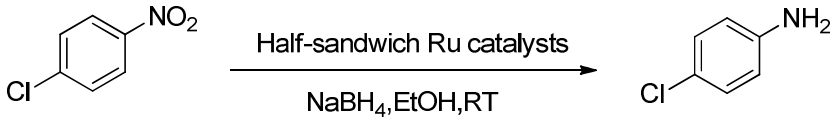
[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$; $wR_2 = [\Sigma w(|F_o^2|-|F_c^2|)^2/\Sigma w|F_o^2|^2]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for ruthenium complexes.

	2a	**2b**	**2c**
Ru1-O1	2.0576(13)	2.0486(14)	2.044(3)
Ru1-N1	2.0857(15)	2.0772(16)	2.078(3)
Ru1-Cl1	2.4368(5)	2.4235(7)	2.4204(17)
Cy_{cent}-Ru[a]	1.6639(1)	1.6675(3)	1.6661(7)
N1-Ru1-O1	86.99(5)	87.05(6)	87.02(12)
N1-Ru1-Cl1	85.88(5)	84.34(5)	84.44(9)
O1-Ru1-Cl1	85.94(5)	84.61(5)	84.57(10)
Cy_{cent}-Ru-O1	124.20(3)	125.38(4)	125.35(1)
Cy_{cent}-Ru-N1	131.33(4)	131.01(5)	131.07(1)
Cy_{cent}-Ru-Cl1	127.89(2)	128.99(2)	128.83(5)

[a] Cy_{cent} is the computed cymene ring carbon centroid.

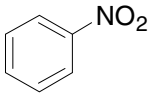
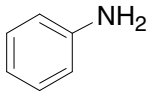
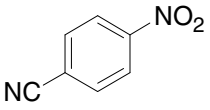
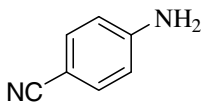
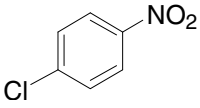
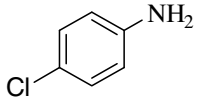
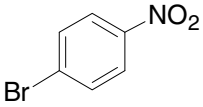
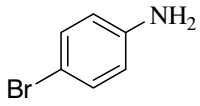
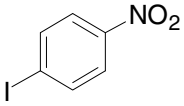
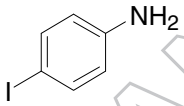
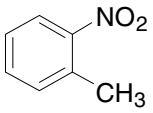
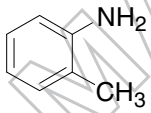
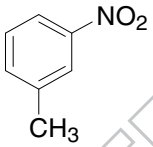
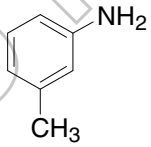
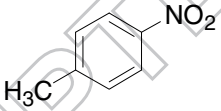
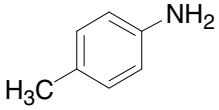
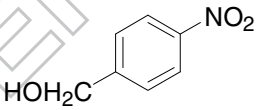
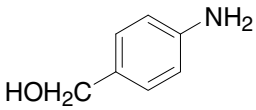
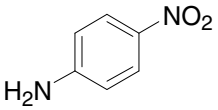
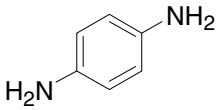
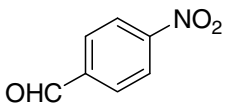
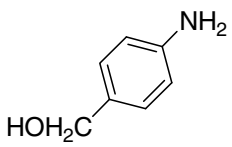
Table 3. Optimization of the reaction conditions for 1-chloro-4-nitrobenzene reduction using ruthenium complexes.[a]

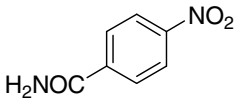
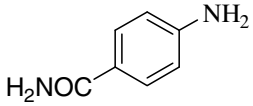


Entry	Catalyst	Solvent	Time (h)	Yield (%)[b]
1	**2a**	EtOH	1	86
2	**2b**	EtOH	1	88
3	**2c**	EtOH	1	90
4	**2d**	EtOH	1	95
5	**2d**	MeOH	9	10
6	**2d**	MeCN	9	40
7	**2d**	H_2O	4	No reaction
8	**2d**	EtOH	2	95[c]
9	**2d**	EtOH	5	90[d]
10	**2d**	EtOH	2	55[e]
11		EtOH	1	No reaction

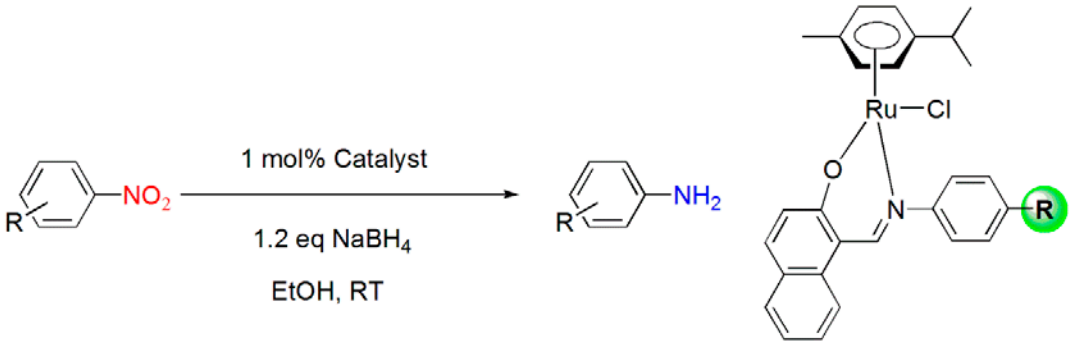
[a] Reaction conditions: 0.3 mmol 1-chloro-4-nitrobenzene, 1.2 mmol $NaBH_4$, Ru catalysts (3 mol %), solvent (2 mL), room temperature; [b] Isolated yield; [c] **2d** (1 mol %); [d] **2d** (0.5 mol %); [e] **2d** (1 mol %), 0.6 mmol $NaBH_4$.

Table 4. Screening of substrates for nitroarene reduction catalyzed by **2d**.[a]

Entry	Substrate	Product	Time (h)	Yield (%)[b]
1			2	88
2			2	97
3			2	95
4			2	92
5			2	90
6			2	92
7			2	92
8			2	95
9			2	90
10			2	96
11			2	95

12			2	95

[a] Reaction conditions: 0.3 mmol nitroarene, 1.2 mmol $NaBH_4$, **2d** (0.003 mmol, 1 mol %), EtOH (2 mL), room temperature. [b] Isolated yield.



R = H, CH_3, Cl, **NO_2**

Catalysts